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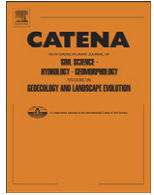
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Cadmium accumulation in six common plant species associated with soils containing high geogenic cadmium concentrations at Le Gurnigel, Swiss Jura Mountains



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ABSTRACT

The uptake of cadmium (Cd) was analyzed for six different perennial plant species growing in a wooded pasture of the Swiss Jura Mountains, where the soils are geogenically enriched in Cd ($4.58 \text{ mg} \cdot \text{kg}^{-1}$ on average ($n = 36$); maximal value: $16.3 \text{ mg} \cdot \text{kg}^{-1}$). The six selected plants — *Hypericum maculatum* (*Hypericaceae*), *Alchemilla xanthochlora* (*Rosaceae*), *Cynosurus cristatus* (*Poaceae*), *Ranunculus acris* (*Ranunculaceae*), *Dactylis glomerata* (*Poaceae*) and *Acer pseudoplatanus* (*Sapindaceae*) — show variable Cd contents among the species and among individuals from the same family (*Poaceae*). Average Cd concentrations in the selected plants are in the $2\text{--}6 \text{ mg} \cdot \text{kg}^{-1}$ range and exceed the maximal Cd concentration tolerated in vegetal feed for animals, which is established at $1 \text{ mg} \cdot \text{kg}^{-1}$. High Cd concentrations in the soil result in a reduction of Cd accumulation in the shoots and a corresponding increase in the roots. This implies that Cd transfer coefficients from the soil/rhizosphere to the plant are inversely proportional to the total Cd concentrations in soils and do not depend on plant species but instead on soil type. Sequential chemical extractions reveal that variations in Cd distribution between the bulk soil and the corresponding rhizospheric soil occur mainly in the Cd-bearing phases, which are exchangeable, bound to carbonates, and associated with organic matter. This is principally due to the incorporation of root exudates, which modify pH and redox conditions of the rhizosphere. Elevated Cd concentrations in the shoots of *A. xanthochlora* (up to $8 \text{ mg} \cdot \text{kg}^{-1}$), *C. cristatus* ($9 \text{ mg} \cdot \text{kg}^{-1}$) and *H. maculatum* ($3 \text{ mg} \cdot \text{kg}^{-1}$) may represent a long-term hazard for livestock and human health since these plants are used either by grazing cattle or for medicinal purposes. On the contrary, *R. acris*, *A. pseudoplatanus*, and especially *D. glomerata* show lower Cd concentrations and are of minor concern with regards to their environmental impact.

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1. Introduction

Cadmium (Cd) is a highly toxic element due both to its enhanced solubility in water and resulting mobility, as well as the low concentrations implied in developing its toxicity (e.g., Benavides et al., 2005; Das et al., 1997; Haghiri, 1973; Lockwood, 1976; Sikka and Nayyar, 2012). Cd-enriched soils are well known to have deleterious effects both on organisms within the soils as well as on the associated vegetation cover, through which it may enter the food chain (e.g., Das et al., 1997; Wahid et al., 2009). Elevated concentrations of Cd and heavy metals in general may impede soil enzyme activity, soil mitochondria growth, litter decomposition and soil respiration (e.g., Lagriffoul et al.,

1998; Tyler et al., 1989; Yao et al., 2003). Plants may suffer from stunting, chlorosis, necrosis, and root and shoot growth limitation through the negative impact of Cd on the uptake, transport and use of biophile elements such as phosphorus (P), calcium (Ca), potassium (K) and iron (Fe) (Das et al., 1997; Liu et al., 2003/2004; Paschalidis et al., 2013; Sikka and Nayyar, 2012). Furthermore, Cd may impede respiration, photosynthesis, water uptake, cell division and induce genetic defects (e.g., Liu et al., 2009; Mohammad et al., 2009; Prasad, 1995; Sanita di Toppi and Gabrielli, 1999).

Apart from the initial Cd concentrations in soils and soil biogeochemical conditions, the accumulation, transport and distribution of Cd within plant systems is dependent on many different factors, such as plant species, root morphology, adsorption of Cd to chelators and peptides, exchange with zinc (Zn), Ca, and manganese (Mn), transpiration rates in leaves, etc. (Das et al., 1997; De Maria et al., 2013; Kashem and Singh, 2002; Tudoreanu and Phillips, 2004).

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In the French and Swiss Jura Mountains, Middle Jurassic (Bajocian) carbonates contain intervals, which are highly enriched in geogenic Cd (Quezada-Hinojosa et al., this volume). As a consequence, associated soils are naturally incorporating this element into their different mineralogical phases (Okopnik, 1997; Benitez, 1999; Prudente, 1999; Prudente et al., 2002; Dubois et al., 2002; Rambeau, 2006; Rambeau et al., 2010; Quezada-Hinojosa et al., 2009, this volume; Efimenko et al., 2014). This is the case at the site called “Le Gurnigel”, which is located in the Jura Mountains, northeast of the “Col de la Vue des Alpes” (canton Neuchâtel, Switzerland). Soils at this site contain Cd concentrations with mean values around $4.6 \text{ mg} \cdot \text{kg}^{-1}$ ($n = 36$) and with a maximal value recorded in the subsoil of $16.3 \text{ mg} \cdot \text{kg}^{-1}$ (Quezada-Hinojosa et al., this volume). These values largely exceed the official Swiss indicative guideline value for soils fixed at $0.8 \text{ mg} \cdot \text{kg}^{-1}$ (Federal Authorities of the Swiss Confederation: OSol, 1998). As such, these soils may represent an environmental risk since the local herbaceous vegetation cover is susceptible to pump and stock this element both in roots and shoots, which are again used by grazing ungulate livestock. Consequently, Cd may gradually enter the food chain and jeopardize animal and human health.

Wermeille (1999) analyzed the total aerial biomass of a large set of local plant species from this area and reported Cd accumulations of up to $9 \text{ mg} \cdot \text{kg}^{-1}$ dry matter (DM), especially in some grass species. With this contribution, we follow up on this research and focus on the individual behavior of six different perennial plant species growing on soils with variable Cd concentrations at the Le Gurnigel site, and analyze Cd accumulations in roots and shoots separately for each species. *Hypericum maculatum* (Hypericaceae), *Alchemilla xanthochlora* (Rosaceae), *Cynosurus cristatus* (Poaceae), *Ranunculus acris* (Ranunculaceae), *Dactylis glomerata* (Poaceae) and *Acer pseudoplatanus* (Sapindaceae) were collected for this purpose. A statistical approach by means of ANOVA Kruskal–Wallis rank sum tests, is used to correlate the data and trace the variability in Cd behavior in plants.

The principal goal of this contribution is to evaluate the dependency of Cd concentrations in the selected plant species on the plant species itself, and on the Cd concentration in bulk and corresponding rhizospheric soils. For the speciation of the Cd concentrations in the soils, a sequential extraction method was used (Quezada-Hinojosa et al., this volume). A further goal was to estimate the degree of hazard each plant species represents for animal and human health.

2. Material and methods

2.1. Site description

The alpine meadow named “Le Gurnigel” (1300 m above sea level) is located on the northern face of the Mont d’Amin (canton Neuchâtel, Switzerland; Fig. 1). The majority of the site overlies Upper Bajocian oolitic limestone (Middle Jurassic). The geomorphology of the site consists of three main hillocks with slopes ranging from 20 to 30%. Soils at the site include thin solums (13–40 cm deep) formed mainly on top of the hill flanks, and deeper soils (80–140 cm deep), which are located in the accumulation zones or coombs formed by the conjunction of two hillocks. The soils at this site consist of Cambisols in general, and more specifically of Hypereutric Cambisols and Cambic Luvisols, which present strong signs of allochthony suggesting that they were formed on aeolian silt deposits of glacial origin (Okopnik, 1997; Quezada-Hinojosa et al., this volume). Fig. 2 shows the six selected soils classified according to the World Reference Base (IUSS Working Group WRB, 2006).

2.2. Plant sampling strategy

The three main soil types were sampled as a function of their degree in evolution, from poorly developed AC-horizon soils to better developed Cambic Luvisols. The three groups of soils were coded as follows:

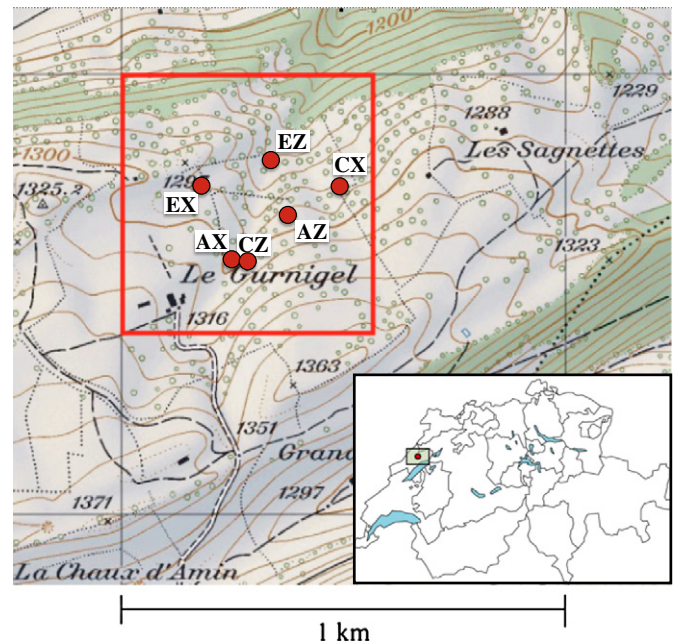


Fig. 1. Topographic map of the Le Gurnigel site with the six sampling points, reproduced with the permission of the Swiss Federal Office of Topography. Inset map of Switzerland is from Wikipedia.org.

A = AC – soil horizons, C = Cambisols – Cambisols (Calcaric), and E = Cambisols – Cambic Luvisols. Okopnik (1997) determined the spatial distribution of Cd at the Le Gurnigel site (Fig. 2c). Using the spatial Cd distribution map Okopnik (1997), two intervals of Cd concentrations were considered: interval X = $1–8 \text{ mg} \cdot \text{kg}^{-1}$ and interval Z = $8–16 \text{ mg} \cdot \text{kg}^{-1}$. The sampling points were therefore coded as AX, AZ, CX, CZ, EX, and EZ (Quezada-Hinojosa et al., this volume: Fig. 1). The exact locations of these points were determined by means of a Garmin ETrex Summit GPS device. The selection of plant species was based on their ubiquity in each of the six sampling points in order to compare the behavior of the same species at each point whenever possible. Following this criterion, six major species of plants were collected (roots and shoots), which are presented in Table 1. In order to control the accuracy of the analyses, three individuals of each species were collected at each sampling point.

All plant individuals were separated from other species, soil particles were washed away and roots were separated from shoots to analyze them individually. We also separated the bulk soil and the soils associated directly with the roots and carefully collected samples of the rhizospheric soil of each of the six plant species. Roots reached a maximal depth of 20 cm (Fig. 2).

2.3. Chemical analyses of trace metals in plants

Roots and shoots were freeze dried by lyophilisation during 63 h at $-40 \text{ }^\circ\text{C}$ and a pressure of 0.05 Pa. Each part was weighed separately in order to measure its respective dried matter (DM) biomass.

Cd concentrations were determined separately in roots and shoots for each plant species as follows: Dried samples were milled using an agate mill and sieved through a 0.5 mm mesh. 150 mg of milled sample were subjected to microwave-assisted acid digestion in PTFE vessels under oxidizing conditions with a mixture composed of 6 ml of concentrated HNO_3 and 2 ml of H_2O_2 . Dissolved samples were subsequently filtered through a 0.45 μm HVLP-Millipore filter before analysis. The filtered solutions were analyzed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS Perkin-Elmer Elan 6100).

2.4. Cd concentration in bulk and rhizospheric soils

Chemical analyses of Cd in bulk and in rhizospheric soil samples were conducted following Method 3051 developed by the U.S. Environmental Protection Agency EPA (1994). 250 mg of dried and grounded sample were subjected to microwave-assisted acid digestion (concentrated HNO₃) and samples were subsequently filtered before analysis. The filtered solutions were analyzed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS Perkin-Elmer Elan 6100).

2.5. Main chemical soil properties

Total organic and mineral-carbon contents were measured in powdered samples by a Rock-Eval⁶™ device. Total carbon and nitrogen contents were also analyzed on powdered samples using an elemental

analyzer Carlo Erba EAL 1108. Soil pH in H₂O was measured using a Metrohm 682 titroprocessor. The cation-exchange capacity (CEC) was measured following the French protocol AFNOR NF X31-130: Soils samples were mixed with a solution of hexaamminecobalt(III) chloride and the concentration of free cobalt ions was measured in a UV spectrometer calibrated to 470 nm.

2.6. Cd distribution in rhizospheric soils

We applied the sequential extraction protocol used by Benitez (1999) and described in Quezada-Hinojosa et al. (this volume). This method allows for the separation and identification of Cd, which is presumed to be distributed in six major fractions: (1) exchangeable (using 0.1 M NaNO₃); (2) carbonates (using 1 M CH₃COONa and buffer at pH 5.0); (3) organic matter (using 0.1 M Na₄P₂O₇); (4) amorphous

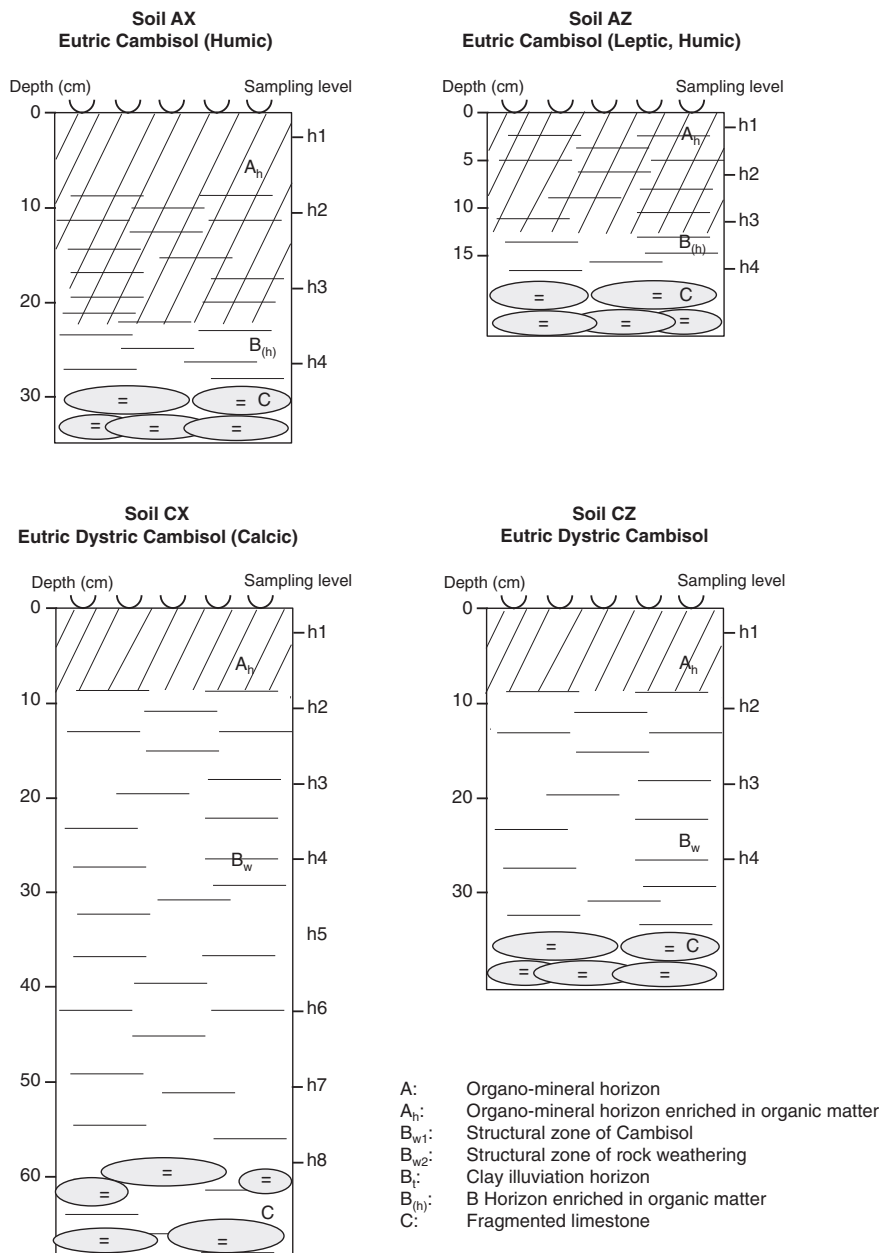


Fig. 2. Soil profiles of the six selected sampling points.

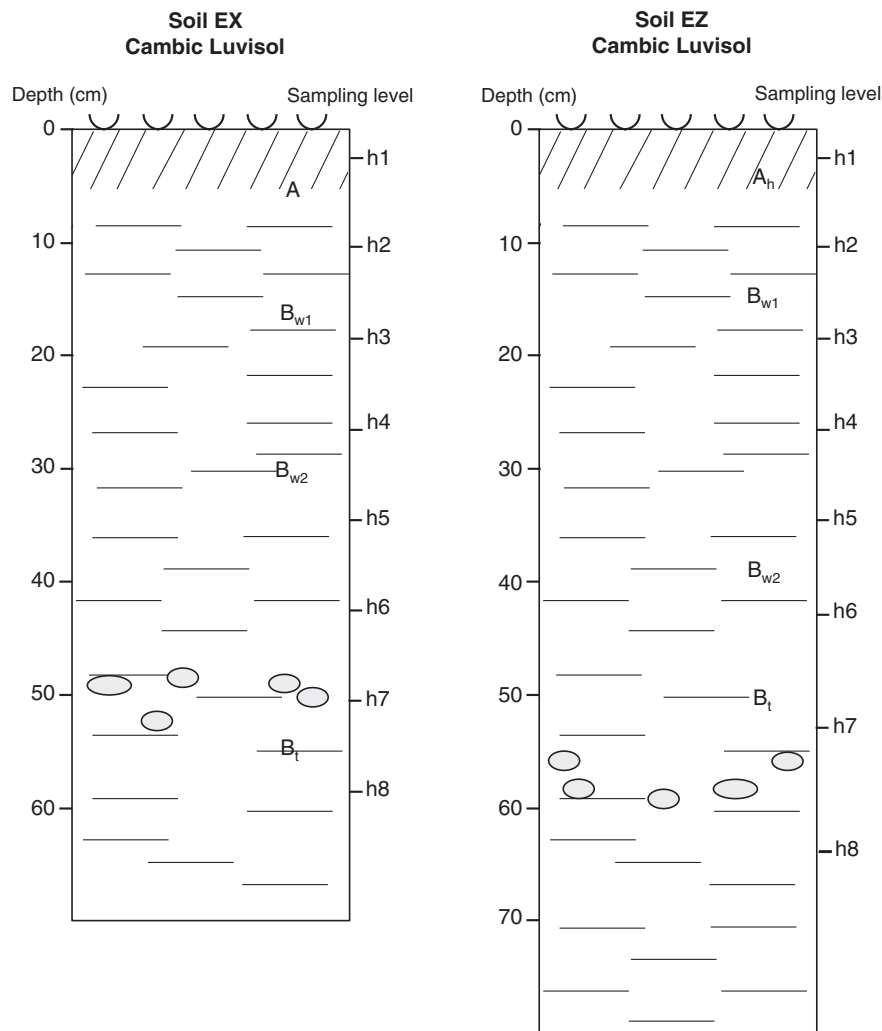


Fig. 2 (continued).

Fe-, Mn-oxyhydroxides (using 0.25 M $\text{NH}_2\text{OH}\cdot\text{HCl}/0.05$ M HCl); (5) crystalline Fe oxides (using 1 M $\text{NH}_2\text{OH}\cdot\text{HCl}/25\%$ CH_3COOH); and (6) residual mineral matrix (using 65% concentrated HNO_3). The filtered supernatants recovered in each extraction step were analyzed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS Perkin-Elmer Elan 6100). In order to assure the accuracy of the results, three replicates for each sample were used in every extraction step.

3. Results

3.1. Total Cd contents in plants

Table 2 summarizes both the arithmetic mean concentrations measured in roots and shoots as well as the concentrations in the entire plants at the six sampling points. As a general rule, Cd concentrations

Table 1
Plant classification.

Plant species	Group	Family	Growth form
Scientific name	Common name		
<i>Hypericum maculatum</i> Crantz	Spotted St. Johnswort	Dicotyledonous <i>Hypericaceae</i> Mangosteen family	Forb
<i>Alchemilla xanthochlora</i> Rothm.	Lady's mantle	Dicotyledonous <i>Rosaceae</i> Rose family	Forb
<i>Cynosurus cristatus</i> L.	Crested dogstail grass	Monocotyledonous <i>Poaceae</i> Grass family	Graminoid
<i>Ranunculus acris</i> L.	Tall buttercup	Dicotyledonous <i>Ranunculaceae</i> Buttercup family	Forb
<i>Dactylis glomerata</i> L.	Orchardgrass	Monocotyledonous <i>Poaceae</i> Grass family	Graminoid
<i>Acer pseudoplatanus</i> L.	Sycamore maple	Dicotyledonous <i>Sapindaceae</i> Maple family	Tree

Table 2
Mean cadmium contents in roots, shoots and total plant.

Soil	<i>Hypericum maculatum</i>			<i>Alchemilla xanthochlora</i>			<i>Cynosurus cristatus</i>		
	[Cd] _{root}	[Cd] _{shoots}	[Cd] _{plant}	[Cd] _{root}	[Cd] _{shoots}	[Cd] _{plant}	[Cd] _{root}	[Cd] _{shoots}	[Cd] _{plant}
	(mg·kg ⁻¹)			(mg·kg ⁻¹)			(mg·kg ⁻¹)		
AX	2.8 ± 1.1	2.5 ± 1.7	2.6 ± 1.5	3.8 ± 1.1	1.2 ± 0.7	3.1 ± 0.8	5.7 ± 1.6	4.5 ± 2.8	4.9 ± 2.3
AZ	2.8 ± 0.5	0.2 ± 0.0	1.1 ± 0.4	9.2 ± 1.3	1.5 ± 0.1	7.0 ± 1.5	8.7 ± 0.1	2.7 ± 0.0	5.0 ± 1.0
CX	4.7 ± 1.0	2.9 ± 0.5	3.2 ± 0.2	14.8 ± 2.0	5.6 ± 0.9	10.3 ± 2.2	7.6 ± 1.7	3.4 ± 1.2	5.4 ± 3.0
CZ	Not found at sampling point			16.2	8.1	13.4	9.9	9.4	9.7
EX	1.5 ± 0.1	0.9 ± 0.2	1.1 ± 0.2	5.6 ± 0.6	3.0 ± 0.4	4.9 ± 0.9	2.9 ± 0.4	1.4 ± 0.2	2.3 ± 0.5
EZ	1.8 ± 0.3	1.5 ± 0.3	1.6 ± 0.3	5.7 ± 0.5	1.2 ± 0.1	4.5 ± 0.9	7.5 ± 1.0	3.0 ± 0.5	4.6 ± 0.2
Soil	<i>Ranunculus acris</i>			<i>Dactylis glomerata</i>			<i>Acer pseudoplatanus</i>		
	[Cd] _{root}	[Cd] _{shoots}	[Cd] _{plant}	[Cd] _{root}	[Cd] _{shoots}	[Cd] _{plant}	[Cd] _{root}	[Cd] _{shoots}	[Cd] _{plant}
	(mg·kg ⁻¹)			(mg·kg ⁻¹)			(mg·kg ⁻¹)		
AX	2.1	0.8	1.2	3.3	0.5	2.2	3.4	0.6	1.5
AZ	6.6 ± 0.7	0.5 ± 0.3	3.3 ± 0.9	2.3 ± 0.2	0.3 ± 0.0	0.9 ± 0.3	5.5 ± 1.7	0.6 ± 0.3	2.1 ± 0.3
CX	4.1 ± 0.8	0.9 ± 0.4	2.2 ± 0.6	2.0 ± 0.2	0.8 ± 0.1	1.3 ± 0.3	Not found at sampling point		
CZ	6.8	2.9	4.5	2.4	0.6	1.4	2.5	0.4	1.4
EX	2.0 ± 0.6	1.7 ± 0.9	1.8 ± 0.8	2.4 ± 0.8	0.6 ± 0.2	1.5 ± 0.2	1.3 ± 0.5	0.7 ± 0.4	1.0 ± 0.5
EZ	2.4 ± 0.4	1.4 ± 0.5	1.7 ± 0.3	1.1 ± 0.2	0.3 ± 0.1	0.6 ± 0.0	3.1 ± 1.0	0.6 ± 0.3	1.7 ± 0.9

in roots are higher than those of the respective shoots for each plant. *A. xanthochlora* (ALXA) shows the highest Cd concentrations for the entire plant (3.1–13.4 mg·kg⁻¹), followed by *C. cristatus* (CYCR) with Cd concentrations in the range of 2.3–9.7 mg·kg⁻¹. *H. maculatum* (HYMA) and *R. acris* (RAAC) present lower Cd contents, with maximal values of 3.2 mg·kg⁻¹ and 4.5 mg·kg⁻¹, respectively. *D. glomerata* (DAGL) and *A. pseudoplatanus* (ACPS) possess the lowest Cd concentrations of all analyzed plants ranging from 0.6 to 2.2 mg·kg⁻¹ in *D. glomerata* and from 1.0 to 2.1 mg·kg⁻¹ in *A. pseudoplatanus*.

Cynosurus appears to be the main Cd accumulator in aerial biomass (maximum value 9.4 mg·kg⁻¹), followed by *A. xanthochlora* (8.1 mg·kg⁻¹), *H. maculatum* (2.9 mg·kg⁻¹) and *R. acris* (2.9 mg·kg⁻¹). *D. glomerata* and *A. pseudoplatanus* present the lowest Cd contents (maximum value of 0.8 mg·kg⁻¹). The Cd concentrations in plants from soil AX and CZ may not be fully representative as data from the triplicates were lost due to technical problems with the ICP-MS during the analyses (Table 2).

3.2. Chemical analyses of rhizospheric and bulk soils

Table 3 summarizes the Cd concentrations measured in the rhizospheric soils of each plant species and the corresponding bulk soils for each profile. Cd concentrations range from 0.3 to 14.3 mg·kg⁻¹. Cd concentrations in the soils decrease in the following order: AZ > CZ > AX > CX > EZ > EX.

Due to the minimal thickness of soil AZ (16.5 cm deep), Cd contents in the rhizosphere equal the mean Cd concentration measured in its deepest level (10 mg·kg⁻¹) rather than the mean value of the topsoil (7.5 mg·kg⁻¹).

The main chemical properties of the topsoils at the six sampling profiles are presented in Table 4. Total organic carbon (TOC) contents are

Table 3
Mean Cd concentrations in rhizospheric and distant soils for all profiles.

Plant species	Cd (mg·kg ⁻¹)					
	AX	AZ	CX	CZ	EX	EZ
<i>H. maculatum</i>	6.7	12.3	4.4	NF	0.3	2.4
<i>A. xanthochlora</i>	4.9	12.0	4.2	6.7	0.4	2.4
<i>C. cristatus</i>	5.9	12.4	4.9	8.1	0.2	2.0
<i>R. acris</i>	4.6	14.3	4.3	7.7	0.5	1.7
<i>D. glomerata</i>	5.1	13.8	3.9	9.6	0.4	2.5
<i>A. pseudoplatanus</i>	5.6	14.3	NF	8.3	0.5	2.0
Bulk topsoil	5.5	7.5	3.8	5.7	0.4	2.2

NF = Plant species not found at the sampling point.

higher in Cambisols AX (6.5%), AZ (6.5%) and CZ (5.6%) than in Cambic Luvisols EX (2.1%), EZ (2.8%). A comparable difference is observed for the cation-exchange capacity (CEC) with the highest values observed in soils AX (17.6 cmol·kg⁻¹), AZ (16.4 cmol·kg⁻¹) and CZ (15.6 cmol·kg⁻¹). The soil pH is rather acidic in the topsoils from the deep soil profiles CX (5.5), EZ (5.5) and especially EX (5.2). All soils are highly decarbonated with low Ca contents, with a minimum value recorded in soil EX (1.9 g·kg⁻¹) and a maximum value of 7.1 g·kg⁻¹ in shallow soil AZ.

3.3. Cd distribution in rhizospheric soils

Sequential extractions were applied to the rhizospheric soils of *A. xanthochlora* and *D. glomerata* in order to evaluate if significant differences are present between the distributions of Cd and trace metals in the rhizosphere of a plant accumulating high quantities of Cd and that of a plant accumulating low quantities of Cd. Moreover, we compared these distributions in two soil groups with different Cd concentrations – the thin Cambisols AX and AZ, and the thick Cambic Luvisols EX and EZ. The results are summarized in Table 5 for *A. xanthochlora* and Table 6 for *D. glomerata*.

Graphical comparisons between mean Cd and trace-metal distributions in the rhizosphere and bulk soil in profiles AX, AZ, EX and EZ are presented for *A. xanthochlora* and *D. glomerata* in Fig. 3 and described in the following.

3.4. Soil AX

Cd bound to the carbonate phase (F2) decreases from 45% in the bulk soil to 32% in the rhizosphere of *A. xanthochlora* and *D. glomerata*. The opposite is observed in the organic-matter phase (F3) where the percentage of Cd rises from 26% in the bulk soil to 32% for *D. glomerata*

Table 4
Main chemical properties of topsoil at the six sampling points.

Soil code	TOC	C _{min}	pH	CEC	C/N	Ca	Fe	Al	Mn
	(%)	(%)		(cmol·kg ⁻¹)		(g·kg ⁻¹)			
AX	6.5	0.4	6.1	17.6	11.9	5.9	47.5	20.6	2.3
AZ	6.5	0.3	5.8	16.4	11.3	7.1	41.1	23.3	1.6
CX	4.7	0.3	5.5	9.1	9.7	2.3	40.3	27.6	1.6
CZ	5.6	0.3	5.8	15.7	10.9	4.7	45.8	26.2	2.3
EX	2.1	0.2	5.2	6.4	12.5	1.9	37.1	23.2	0.8
EZ	2.8	0.2	5.5	8.4	11.8	2.5	42.1	25.2	2.1

Table 5
Distribution of Cd in rhizospheric soil of *Alchemilla xanthochlora* collected in Cambisols AX, AZ and Cambic Luvisols EX, EZ.

Soil fraction	Rhizospheric soil of <i>Alchemilla xanthochlora</i>			
	Percent distribution of Cd (%)			
	Soil AX	Soil AZ	Soil EX	Soil EZ
F1 Exchangeable	0.8	0.3	21.4	5.8
F2 Carbonates	32.4	29.9	39.7	48.8
F3 Organic matter	36.0	38.5	14.9	17.8
F4 Amorphous oxyhydroxides	18.0	18.2	13.2	9.6
F5 Crystalline Fe oxides	10.5	11.5	10.8	14.8
F6 Residue	2.3	1.6	0.0	3.2
Recovery (%)	118.8	99.6	105.7	88.9

and 36% for *A. xanthochlora*. Rather small changes are observed for amorphous oxyhydroxides (F4) where Cd rises from 15% to 18.5% in both rhizospheres. The exchangeable fraction (F1) does not seem to be greatly modified with a reduction from 2% to 1.4% (*D. glomerata*) and 0.8 (*A. xanthochlora*). Cd associated with Fe-oxides remains constant while Cd residing in the silicate matrix slightly increases from 1.5% to 2.4% in the rhizosphere of both plants.

3.5. Soil AZ

This soil presents changes in its Cd distribution similar to that in soil AX. The Cd percentage in the carbonate fraction diminishes from 51% to 34% for *D. glomerata* and 30% for *A. xanthochlora*. Cd-bound to organic matter rises from 22% to 38.5% (*A. xanthochlora*) and 49% (*D. glomerata*), respectively. Cd in amorphous oxides doubles from 9% to 18% in both rhizospheres. The exchangeable fraction is reduced from 2% to 1% in *D. glomerata* and 0.3% in *A. xanthochlora*. Cd in the residual matrix is reduced from 4% to nearly 1.5% in the rhizosphere. Cd in crystalline Fe-oxides remains constant.

3.6. Soil EX

The exchangeable Cd rises considerably if compared to the other soils, increasing from 8.5% in bulk soil to 16% in rhizospheric soil of *D. glomerata* and 21% in *A. xanthochlora*. The carbonate phase remains rather constant. Cd bound to organic matter decreases from 15% to 12% in *D. glomerata* but remains constant in *A. xanthochlora*. Cd in amorphous oxyhydroxides is reduced from 20% to 12% for *A. xanthochlora* and to 5% in *D. glomerata*. Cd in Fe-oxides diminishes from 20% to 12% in both rhizospheres. The rhizosphere of *D. glomerata* presents 5% Cd in the residual phase while it is absent in its bulk soil and in that of *A. xanthochlora*.

Table 6
Distribution of Cd in rhizospheric soil of *Dactylis glomerata* collected in Cambisols AX, AZ and Cambic Luvisols EX, EZ.

Soil fraction	Rhizospheric soil of <i>Dactylis glomerata</i>			
	Percent distribution of Cd (%)			
	Soil AX	Soil AZ	Soil EX	Soil EZ
F1 Exchangeable	1.4	1.1	16.4	0.0
F2 Carbonates	33.2	34.4	48.2	32.2
F3 Organic matter	32.9	48.7	12.0	28.9
F4 Amorphous oxyhydroxides	18.7	8.8	5.2	19.2
F5 Crystalline Fe oxides	11.4	5.8	12.9	17.6
F6 Residue	2.4	1.2	5.2	2.1
Recovery (%)	95.4	102.9	114.3	94.2

3.7. Soil EZ

Exchangeable Cd appears only in the bulk soil (2.5%) and in the rhizospheric soil of *A. xanthochlora* (5.8%). Cd bound to the carbonate fraction is higher in *A. xanthochlora* (50%) than in bulk soil (44%). Cd bound to organic matter and to residual matrix remains on a level of 29% in *D. glomerata* and 18% in *A. xanthochlora*. Cd in amorphous oxyhydroxides varies from 13% in bulk soil to 19% (*D. glomerata*) and 10% (*A. xanthochlora*), respectively. Cd bound to Fe-oxides does not show a significant variation.

4. Discussion

4.1. Cd uptake by plants

In a first approach, we plotted average Cd concentrations for all plants, with no distinction of species, against Cd contents in the six soils (Fig. 6a). Global concentrations of Cd in plants are in the range of 2–6 mg·kg⁻¹ for dried matter (DM). As such, these levels exceed the generally accepted tolerance level for edible plant products, such as wheat, rice, soybean, and peanut, which is fixed at 0.2 mg·kg⁻¹ (Federal Authorities of the Swiss Confederation: OSEC, 1995; joint FAO/WHO food standard program; WHO, 2002). They also exceed the maximal Cd concentration tolerated in plant feed for animals, established at 1 mg·kg⁻¹ (Federal Authorities of the Swiss Confederation: OSEC, 1995). However, these concentrations are within the range of limit values of 5–10 mg·kg⁻¹ dry matter for plants and are lower than the critical values, which range from 10 to 20 mg·kg⁻¹ dry matter (Agence de l'Environnement et de la Maîtrise de l'Energie, 2010). It may be noted here that statistically significant toxic effects of Cd on humans are already signaled at levels as low as 0.3 mg·kg⁻¹, in the case of long-term exposure (e.g., in rice in east Asiatic countries; Ishihara et al., 2001; cf. also Satarug et al., 2003).

It is expected that a rise in the concentration of Cd in a given soil would produce a stronger accumulation in a plant growing on it. This may be true for the increasing concentrations in the sequence of 0.5, 2.6, and 4.3 mg·kg⁻¹ observed in soils EX, EZ, and CX, respectively. However, plants from soils AX and AZ, which contain higher levels of Cd in the topsoil (5.5 and 6.7 mg·kg⁻¹, respectively), appear to accumulate lower quantities of Cd than their counterparts in soil CX and soil CZ (average Cd contents of 5.7 mg Cd·kg⁻¹). Care should be taken with the high standard deviation of plants in soil CZ (Fig. 4a) due to the lack of triplicates.

Cd uptake by plants is a process controlled not only by the concentration and speciation of the element in the soil solution, but also by the movement of the element from the bulk soil to the root surface, its transport from the root surface into the root, and its translocation from the root to the shoots (Chaney and Giordano, 1977; Alloway, 1995; Tudoreanu and Phillips, 2004; De Maria et al., 2013). Wild (1988) observed that plant uptake of mobile ions in the soil solution is largely determined by the total quantity of this ion in the soil. However, in the case of strongly adsorbed ions, absorption rates are more dependent upon the amount of root produced and result in yield reduction (cf. also Tudoreanu and Phillips, 2004). Fig. 4b–c presents global Cd concentrations in roots and shoots as a function of total Cd concentrations in the topsoil. As a general rule, roots accumulate higher Cd concentrations than shoots (Sauerbeck, 1991; Cieslinski et al., 1996; Lehoczyk et al., 1996; De Maria et al., 2013). The varietal influence may depend on whether a given plant species retains Cd taken up in the roots or translocates it to the shoots as it has been demonstrated in maize plants (Florijn and van Beusichem, 1993; Chizzola and Lukas, 2005).

It has been observed in rice and strawberries that a rise in the concentration of Cd in the soil progressively reduces the transport of Cd toward shoots. In this way, plants growing in non-polluted soils may easily transfer ions from the roots toward the leaves. The opposite occurs in Cd-rich soils where roots tend to accumulate higher quantities

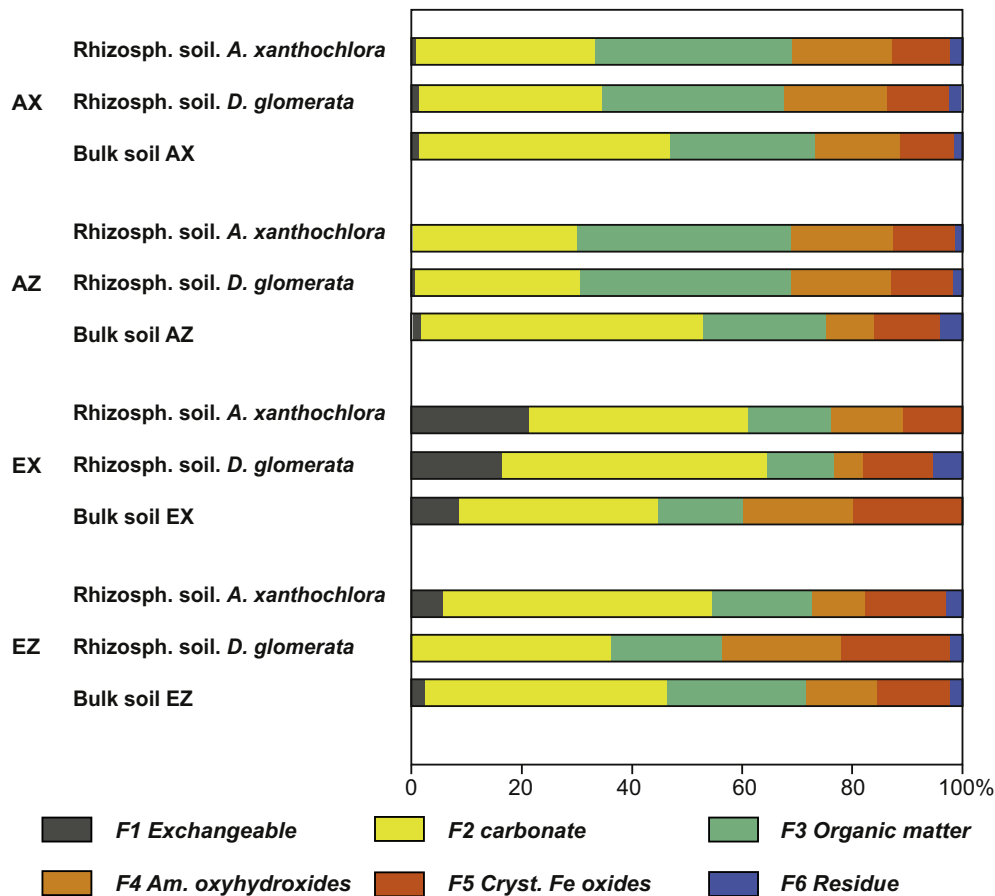


Fig. 3. Mean percent distribution of Cd extracted in rhizospheric and bulk soils. Data are compared between *Alchemilla xanthochlora* and *Dactylis glomerata* in soil profiles AX, AZ, EX and EZ.

of Cd while only a low percentage is transferred to shoots (Cieslinski et al., 1996; Nocito et al., 2011). Plants show a similar behavior with regards to micronutrients such as Cu, Fe, Mn and Zn (Kataba-Pendias and Pendias, 1992; Alloway, 1995; Das et al., 1997; Ramos et al., 2002; Sejeroglu et al., 2008). The supply of a micronutrient may increase until a lower critical concentration level is reached. Below this level, the plant grows normally and no deficiencies occur in yield production. Above the upper critical concentration level, a yield reduction occurs due to toxicity (Haghiri, 1973; Alloway, 1995; Lagriffoul et al., 1998). When growing in soils with high Cd concentrations, the plant may control its Cd household by stocking the excess Cd in roots (Cieslinski et al., 1996; Nocito et al., 2011). This is the case in soils AX and AZ where Cd concentrations in shoots drop (from $2.7 \text{ mg} \cdot \text{kg}^{-1} \text{ DM}$ in soil CX to $2.2 \text{ mg} \cdot \text{kg}^{-1} \text{ DM}$ and $1 \text{ mg} \cdot \text{kg}^{-1} \text{ DM}$, respectively (Fig. 4c). This mechanism of detoxification may well depend on genetic differences within plant species (Wermeille, 1999).

4.2. Cd uptake by plants as a function of species identity

Fig. 5 depicts global Cd concentrations measured for each plant species as a function of the total Cd concentration in the topsoil. *A. xanthochlora* appears with the highest concentrations followed by *C. cristatus* (Table 2). It has been reported that the transfer of Cd from the soil into the plant may vary greatly with the plant species and even with the variety or genotype within a given species (Malko, 2002; Schneider et al., 2002). This is the case for *C. cristatus* and *D. glomerata*, both of the family *Poaceae*, which behave differently in the same soil and

show two extremes, with *C. cristatus* as an important and *D. glomerata* as a poor Cd accumulator (Table 2).

Fig. 5 shows that Cd levels in all plant species gradually increase until they reach a maximum value in soil CX. They consequently drop to lower levels in soil AX as the detoxification mechanisms described above may stop the transfer of Cd toward the shoots. The Cd uptake by plants in soil AZ rises again, which is probably due to the high levels present in the rhizosphere (over $10 \text{ mg} \cdot \text{kg}^{-1}$). In this case the Cd is stocked mainly in the roots.

4.3. Cd uptake by plants as a function of soil type

Fig. 6a–b depicts Cd concentrations in each plant species plotted against soil type. A progressive increase in Cd uptake is observed for *A. xanthochlora* going from soils AX, AZ, CX to CZ, where a maximum value of $13.4 \text{ mg} \cdot \text{kg}^{-1}$ is reached. This may be explained by the decreasing concentrations in Cd as discussed before. Cd levels in *A. xanthochlora* decreases in soils EX and EZ, which is probably due to their lower Cd concentrations. A similar situation is observed for *C. cristatus*, with a maximum value of $9.7 \text{ mg} \cdot \text{kg}^{-1}$ in soil CZ. *H. maculatum* appears to follow the same trend though the values do not change as clearly as for the two previous potential accumulators. *R. acris*, *A. pseudoplatanus*, and *D. glomerata* do not follow a discernible trend.

Table 7 summarizes estimations of Cd percentage in roots and shoots of each plant species for the six soil profiles. Soils are arranged by increasing Cd concentrations in the soil in order to compare the changes in Cd distribution between roots and shoots. The soil composition, pH,

organic matter, CEC and available mineral elements and interdependencies between these parameters may decrease or increase the availability of Cd for plants (Chizzola and Lukas, 2005; Kirkham, 2006). Plescher et al. (1995) reported that at lower soil pH, higher Cd bioaccumulation has been recorded in various medicinal plants, including a variety of *H. maculatum*. Chizzola and Lukas (2005) found that in regression analyses, soil pH, soil organic carbon and soil Cd content were the main factors influencing Cd accumulation in the plant shoots. Despite these observations, Wermeille (1999) found that the pH of Le Gurnigel soils does not have a direct influence on Cd uptake by plants.

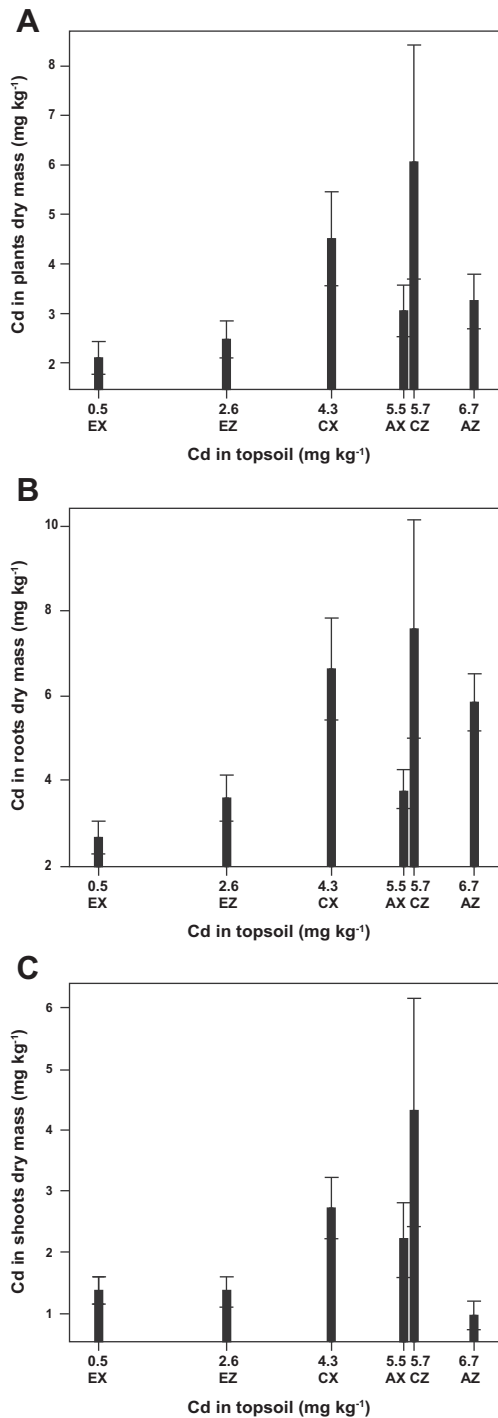


Fig. 4. Global Cd concentrations in plants measured in (a) entire plant; (b) roots; (c) shoots.

4.4. Transfer coefficients

The soil–plant transfer coefficient is obtained from the ratio of each detected metal concentration in plant tissues to that in soil (Kloke et al., 1984). It quantifies the relative differences in bioavailability of soil metal to plant and is a function of both soil and plant properties (Alloway, 1995). Soil–plant transfer coefficients for Cd vary usually between 1 and 10 (Kloke et al., 1984; Alloway, 1995).

4.4.1. Transfer from topsoil to rhizosphere

One of our goals was to determine whether the transfer of Cd from the topsoil to the rhizosphere depends on the total Cd concentration in the topsoil. Following the definition of a transfer coefficient, we calculated the transfer ratio from the bulk soil (topsoil) to the rhizosphere as $[Cd]_{rhiz}/[Cd]_{topsoil}$ and plotted the obtained ratios as a function of Cd in the bulk topsoil in Fig. 7.

A significant linear regression (p -value = 2.319×10^{-7} , R^2_{adj} = 0.5584) and a positive Spearman's rank correlation (p -value = 1.814×10^{-10} ; ρ = 0.851) suggest that there exists a direct relation between these two variables. A rise in the Cd levels in the topsoil may produce an augmentation (or decrease in depletion) of Cd in the rhizosphere.

With regards to the influence of the plant species, a Kruskal–Wallis rank sum test (p -value = 0.9911) suggests that a clear relationship between the transfer of Cd from the topsoil to the rhizosphere and species identity is lacking, and that the physicochemical soil properties and changes therein largely determine the degree of Cd mobilization across the bulk soil–rhizosphere interface.

In order to determine whether the transfer of Cd from the topsoil to the rhizosphere depends on specific Cd-bearing fractions of the topsoil, linear regressions were applied by which the Cd transfer ratio as a function of Cd concentration in each soil fraction was kept as a variable (Fig. 8). It results that Cd associated with crystalline Fe-oxides, the residual phase, the exchangeable and carbonate phases provides significant fractions, which explain 80% of the variance. Organic matter has a reduced effect probably due to the binding of Cd to organic substances in the soil. Chizzola and Lukas (2005) reported that higher organic carbon content in the soil may result in lower Cd concentrations in the plant. Variations in the Cd distribution in rhizospheric soils (Fig. 3) are mainly observed for the first three fractions and especially for the exchangeable and carbonate fractions. Changes in Cd concentrations bound to these fractions may therefore depend on a complex combination of plant physiological characteristics, initial Cd concentrations in

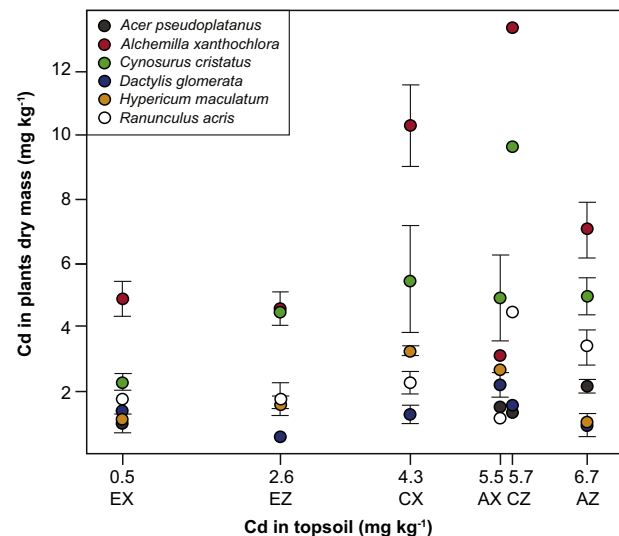


Fig. 5. Global Cd concentrations in plants separated by species identity.

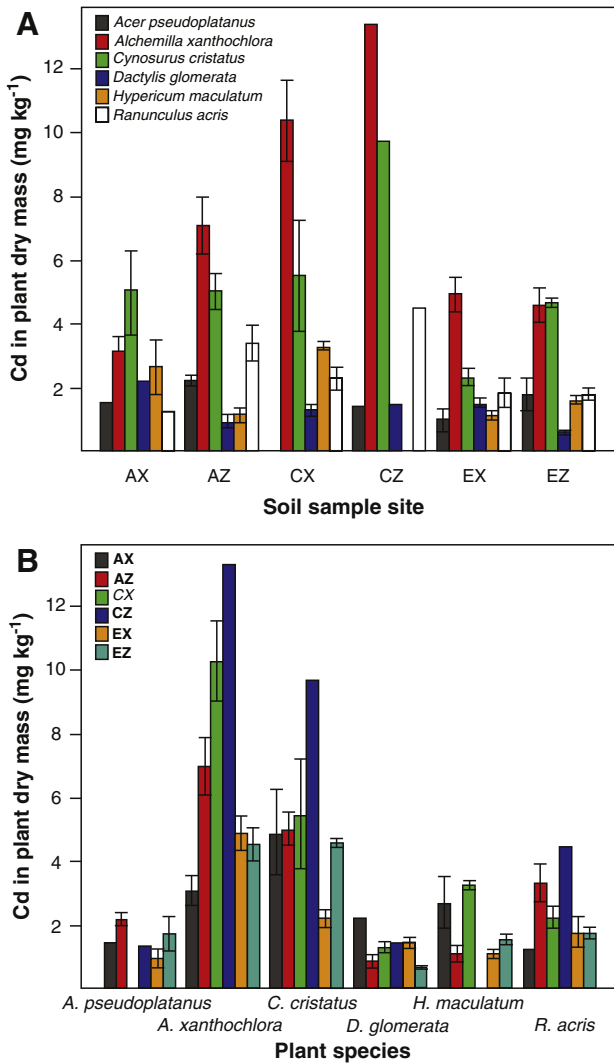


Fig. 6. Cd concentration in plants as a function of (a) soil type; (b) species identity.

Table 7

Estimated percentages for the Cd distribution in roots and shoots. Soils are arranged by increasing mean Cd concentrations in the topsoils.

Soil	Mean Cd mg·kg ⁻¹	<i>Hypericum maculatum</i>		<i>Alchemilla xanthochlora</i>		<i>Cynosurus cristatus</i>	
		Cd _{roots} %	Cd _{shoots} %	Cd _{roots} %	Cd _{shoots} %	Cd _{roots} %	Cd _{shoots} %
EX	0.5	60.5	39.5	89.1	10.9	79.2	20.8
EZ	2.6	26.1	73.9	96.3	3.7	63.4	36.6
CX	4.3	15.4	84.6	81.2	18.8	45.6	54.4
AX	5.5	32.6	67.4	86.9	13.1	52.8	47.2
CZ	5.7	Not found		78.4 ^a	21.6 ^a	62.0 ^a	38.0 ^a
AZ	7.0	93.4	6.6	96.1	3.9	73.4	26.6
Soil	Mean Cd mg·kg ⁻¹	<i>Ranunculus acris</i>		<i>Dactylis glomerata</i>		<i>Acer pseudoplatanus</i>	
		Cd _{roots} %	Cd _{shoots} %	Cd _{roots} %	Cd _{shoots} %	Cd _{roots} %	Cd _{shoots} %
EX	0.5	47.0	53.0	84.0	16.0	60.5	39.5
EZ	2.6	60.2	39.8	71.7	28.3	77.5	22.5
CX	4.3	70.4	29.6	69.7	30.3	Not found	
AX	5.5	58.3 ^a	41.7 ^a	91.1	8.9	74.0	26.0
CZ	5.7	59.9 ^a	40.1 ^a	76.6 ^a	23.4 ^a	85.8 ^a	14.2 ^a
AZ	7.0	85.1	14.9	81.3	18.7	88.6	11.4

^a Data calculated with only one individual.

the soil, and soil properties. Organic matter has a mixed influence on the transfer of Cd from the soil to the rhizosphere because in the rhizosphere this phase receives appreciable amounts of organic material from the roots, including exudates, mucilage, sloughed-off cells and their lysates. This is associated with a general rise in the microbial and biochemical activity (Dong et al., 2007). The addition of organic material in the rhizosphere will either dilute or increase Cd percentages derived from bulk soils.

Amorphous oxyhydroxides appear to have a reduced influence because they are less important as a Cd-bearing phase. Cd percentages in these compounds may eventually increase when roots enter in contact with the subsoil as is the case at the thin soil sites. This may explain the increase in Cd bound to amorphous oxides observed in the rhizospheres of soil AZ. With regards to the thicker soils, the presence of Cd bound to this phase mainly depends on whether the roots reach the subsoil horizons rich in Cd adsorbed to amorphous oxyhydroxides. Thicker soils with lower pH and low CEC may favor the presence of bioavailable Cd with higher contents in the easily exchangeable phase. Furthermore, carbonates and organic matter will still be fractions susceptible to release Cd for plant uptake, especially in the case of a decrease of the pH in the rhizosphere. pH and redox conditions in the rhizosphere are not sufficient to mobilize Cd-bound to crystalline Fe-oxides (fraction 5) and residual matrix (fraction 6).

4.4.2. Transfer from rhizosphere to plants

The transfer coefficient of Cd from the rhizosphere to plants [Cd]_{plant}/[Cd]_{rhiz} is presented in Figs. 9 and 10 as a function of total Cd concentrations in the topsoil and the rhizosphere. We observe in both figures that the transfer coefficient is inversely proportional to both concentrations. It was already discussed that increasing concentrations of Cd in soils will lead to a decrease in its transfer rate toward the upper parts of plants.

4.4.3. Transfer from topsoil to plant

The transfer coefficient of Cd from topsoil to plant [Cd]_{plant}/[Cd]_{topsoil} is presented in Fig. 11 as a function of total Cd concentrations in the topsoil. As in Fig. 9, the relation between the transfer from soil to plant is inversely proportional to Cd concentrations in the soil.

In order to determine whether the transfer from topsoil to plant depends on species identity, we applied a Kruskal–Wallis rank sum test. The obtained p-value = 0.0002841 (<0.05) suggests that the species identity plays an important role in Cd uptake.

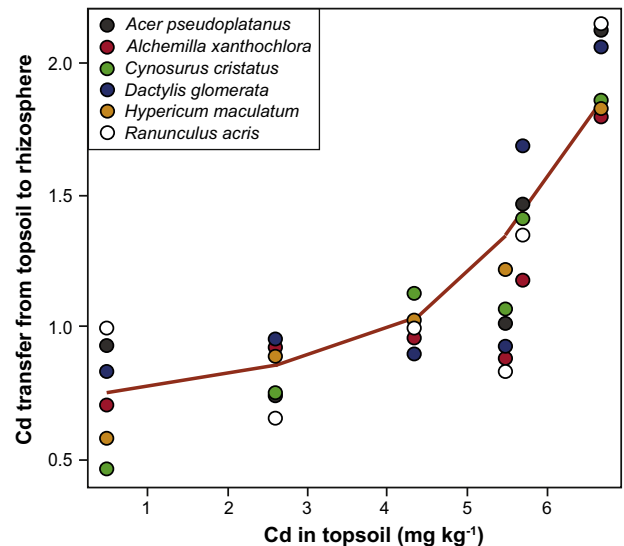


Fig. 7. Effect of total Cd concentrations in the topsoil on the transfer from topsoil to the rhizosphere.

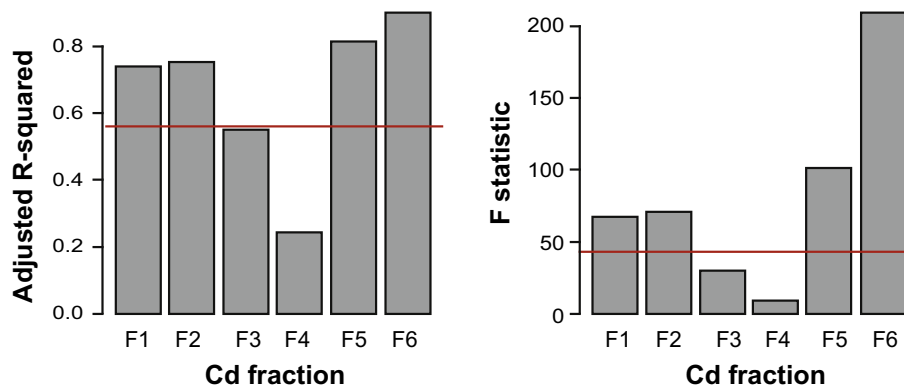


Fig. 8. Evaluation of linear regressions between Cd transfer from the topsoil to the rhizosphere and Cd concentrations in each soil-bearing fraction. The horizontal red line corresponds to the R^2_{adj} coefficient (right) and F-value (left).

The comparable distributions of the box plots of *A. xanthochlora* and *C. cristatus* (Fig. 12) confirm that these two plants have strong abilities to absorb and transfer Cd to the plant tissues since their coefficients reach the highest values, whereas the coefficient of *D. glomerata* is the lowest. A further Kruskal–Wallis rank test (p -value = $3.606 \cdot 10^{-8}$; Fig. 13) confirms that the transfer from the topsoil to the plant depends on the soil type. Soil EX shows the highest transfer rate even though the plants growing in this soil record low concentrations compared to those of the other soils. This may be explained by the low CEC value ($6.4 \text{ cmol} \cdot \text{kg}^{-1}$), the low pH (5.2) and the high percentages of exchangeable Cd in the rhizosphere (up to 21%) despite the low Cd concentrations in the topsoil ($0.4 \text{ mg} \cdot \text{kg}^{-1}$).

It has already been observed that plants growing on Cd-contaminated soils may present lower Cd bioaccumulation rates than when growing on soils with low Cd concentrations (Plescher et al., 1995; Hooda et al., 1997). In the evaluation of bioaccumulation rates, one has to consider, however, that high rates may result for plant samples low in Cd when the corresponding soils are very low in Cd (Chizzola and Lukas, 2005).

4.5. Risk assessment of Cd in plants

Plants at the Le Gurnigel pasture are revealed to accumulate rather high levels of Cd in their roots and shoots. The main risk is represented

by three species, which happen to occur in high density in comparison to the other plant species selected here and which are used either by grazing livestock or as medicinal plants to treat specific health problems. The Cd concentrations observed in these plants exceed the official maximum concentration for animal feed fixed at $1 \text{ mg} \cdot \text{kg}^{-1}$ and the tolerance limit value for cattle feed ($0.5 \text{ mg} \cdot \text{kg}^{-1}$). However, the measured concentrations do not surpass the concentration level fixed at $30 \text{ mg} \cdot \text{kg}^{-1}$ (Federal Authorities of the Swiss Confederation: OSEC, 1995), above which a toxicity risk for animals is given. Yet they are likely to menace animal and human health on a long-term period by entering the food chain.

A. xanthochlora was found to accumulate the highest cadmium concentrations. Mean values are in the $3\text{--}10 \text{ mg} \cdot \text{kg}^{-1}$ range. 81–96% of Cd is accumulated in roots (maxima $15 \text{ mg} \cdot \text{kg}^{-1}$) though shoots present also important Cd contents (maxima $6 \text{ mg} \cdot \text{kg}^{-1}$). As such, this plant represents a serious threat to human health through the forage–milk–cheese chain, since it is one of the dominant species in mountain grassland. Furthermore, it is used for its medicinal virtues. It has astringent and anti-inflammatory properties, controls bleeding and is taken as an infusion for menstrual and menopausal problems. It is also possible to use young leaves of this plant to prepare a variety of “salad of bitters”.

C. cristatus is a typical grassland species used by grazing ungulate livestock. Cows and sheep eat the young leaves eagerly, but leave the stiff, hard stems. It withstands the cold and drought and remains green during the winter. Since shoots of this plant contain Cd levels

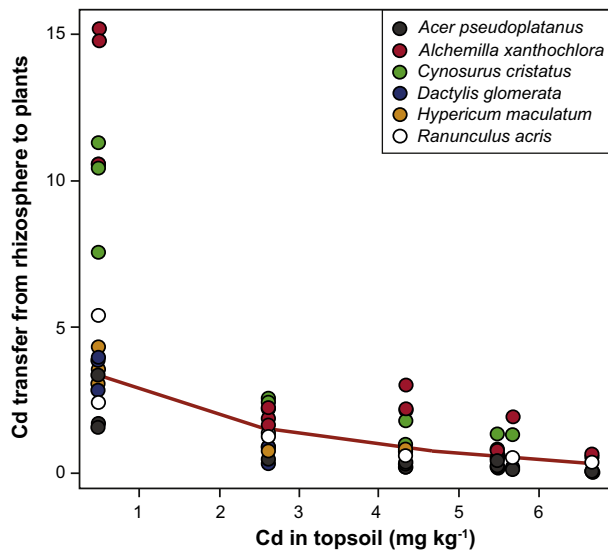


Fig. 9. Effect of total Cd concentrations in the topsoil on the transfer of Cd from the rhizosphere to the plants.

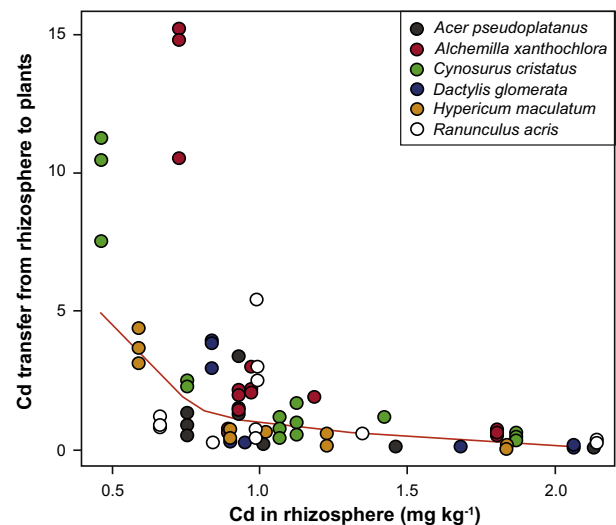


Fig. 10. Effect of total Cd concentrations in the rhizosphere on the transfer of Cd from the rhizosphere to the plants.

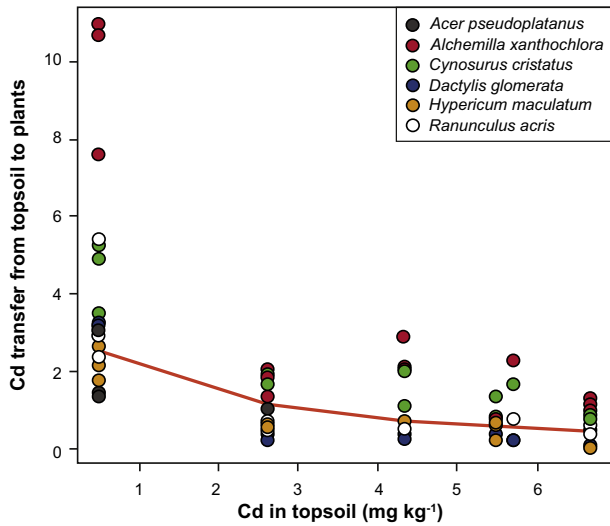


Fig. 11. Effect of total Cd concentrations in the topsoil on the transfer of Cd from the topsoil to the plants.

which range from 1.4 to 4.5 mg·kg⁻¹, there exists a possible menace for animals by the long-term input of Cd to the food chain.

H. maculatum is not grazed upon by cattle, and occurs commonly in fallows or undergrazed microsites. It is used as a remedy since ancient times, in particular to treat ulcers, burns, wounds, abdominal pains and bacterial diseases. Shoots of this plant contain Cd concentrations of up to 3.0 mg·kg⁻¹, hence providing a risk for human health.

Shoots of *R. acris* possess Cd concentrations in the 0.5–2.0 mg·kg⁻¹ range. Even though these concentrations are somehow higher than the official limit values for animal feed, the plant is not considered of risk since cattle pass it up (but may be a problem in hayfields). This plant, as well as other buttercups, contains ranunculin, which breaks down to the toxin protoanemocin, a chemical that can cause dermatitis and vomiting.

D. glomerata is a plant known for its pastoral value. The low concentrations of Cd in shoots (up to 0.8 mg·kg⁻¹) render this plant of minor concern.

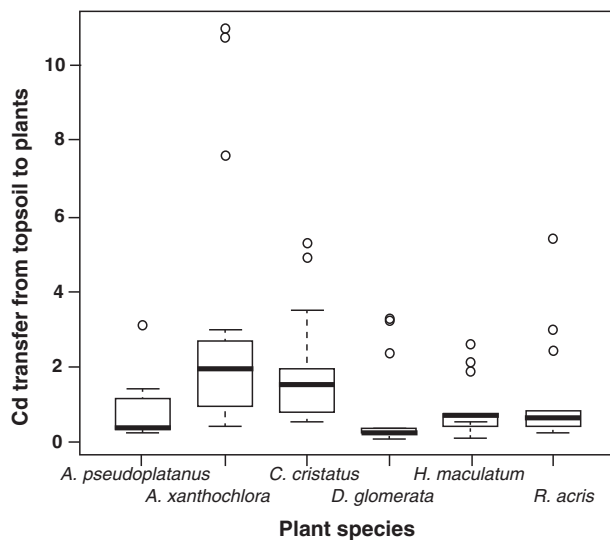


Fig. 12. Box diagram showing the effect of species identity on the transfer from topsoil to plant.

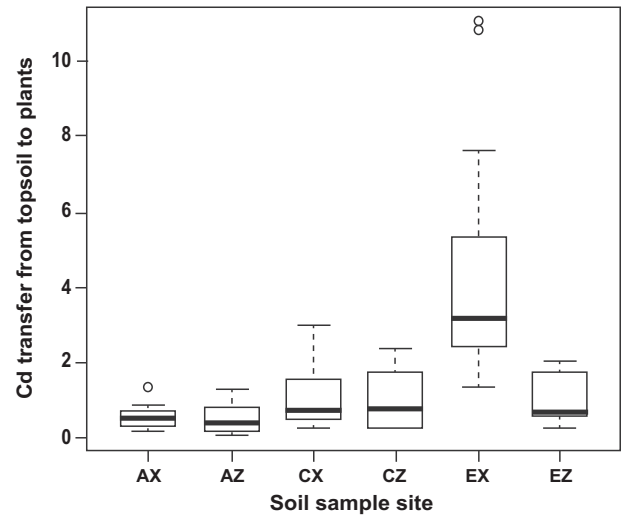


Fig. 13. Box diagram showing the effect of soil type on the transfer from the topsoil to the plant.

A. pseudoplatanus presents rather low concentrations in Cd in their stems and leaves (0.7 mg·kg⁻¹), though the root is able to uptake larger quantities of Cd (up to 5.5 mg·kg⁻¹). The plant samples analyzed here do not present any signs of visible toxicity in the young leaves and root itself.

5. Conclusions

Plants growing at the Le Gurnigel pasture are susceptible to accumulate high levels of geogenic Cd. The six species analyzed here – *H. maculatum*, *A. xanthochlora*, *C. cristatus*, *R. acris*, *D. glomerata* and *A. pseudoplatanus* – show global mean Cd concentrations, which range from 2 to 6 mg·kg⁻¹. The variability in Cd concentrations is shown here to relate to soil type and its Cd content. The Cd concentrations in plants measured here exceed the maximal concentration tolerated in vegetal feed for animals (1 mg·kg⁻¹). As a general rule, relative to the mean concentrations, the percentages of Cd concentrations in roots are higher than in shoots and appear to depend on Cd concentrations in soil, though the proportions may strongly vary from one species to another. Nevertheless, shoots of some plants (*A. xanthochlora*, *C. cristatus*, *H. maculatum*) may reach maximum concentrations in the 3–13 mg·kg⁻¹ range, depending on species identity. As such, these plant species may represent a long-term hazard for animals and human health given that they are used either by grazing livestock or for medicinal purposes. *R. acris*, *A. pseudoplatanus*, and *D. glomerata* are of lower concern.

In extrapolating from our observations, we suggest that plants in soils containing up to 4 mg Cd·kg⁻¹ may develop a tendency to progressively accumulate Cd in their different parts. However, when growing in soils with higher concentrations, plants are thought to use a detoxification mechanism which induces them to stock Cd in roots by a series of organic-ligand complexation mechanisms, and as such reduce the transport of Cd ions toward the shoots, thereby also reducing the yield production. This may explain the inverse relationship between Cd transfer coefficients from the bulk soil/rhizosphere to the plants and the total Cd concentration in soils. The transfer of Cd from the topsoil to the rhizosphere does not appear to depend on species identity, but on soil type and the physicochemical changes at the soil–rhizosphere interface. The exchangeable, carbonate and organic-matter fractions associated with Cd appear mainly affected by biogeochemical activity in the rhizosphere, thereby potentially increasing the bioavailability of Cd.

Acknowledgments

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